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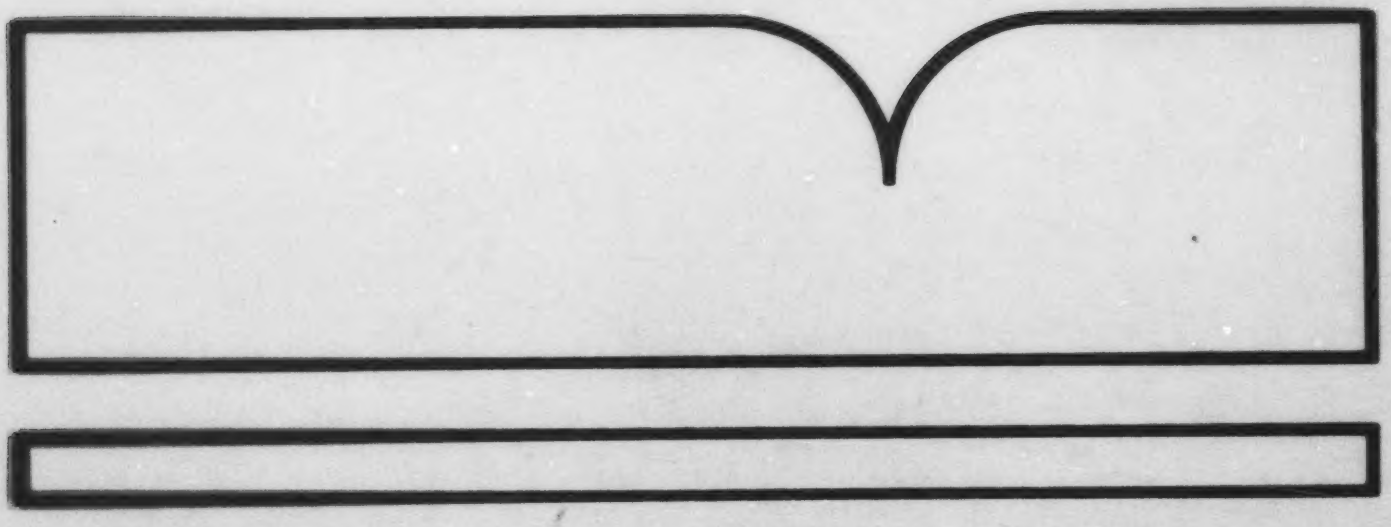

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A nitric acid diffusion denuder made of nylon was operated in Riverside, CA, Houston, TX, and Claremont, CA. The pre-exponential and diffusion coefficients for the first term of the Gormley-Kennedy equation were estimated by regressing the log (mass deposited) against the axial distance from the entrance of the denuder. The field study average values of the two coefficients were compared by the two-tail t-test to the average values for the $HNO_3$-Air system determined in the laboratory; the test revealed that the means of the diffusion coefficients have probabilities $\leq 0.03$ of being equal. The nitrate ion mass patterns in the denuder for the field cases do not adhere to the Gormley-Kennedy model applied to the simple $HNO_3$-Air system. The source of excess nitrate deposited in the nylon tube could not be identified by this analysis. Candidate sources are deposition of gaseous N-compounds (analyzed as nitrate) other than nitric acid and evaporation of nitric acid from particles during transit in the denuder tube.

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# NITRIC ACID–NITRATE AEROSOL MEASUREMENTS BY A DIFFUSION DENUDER: A PERFORMANCE EVALUATION

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**Abstract**—A nitric acid diffusion denuder made of nylon was operated in Riverside, CA, Houston, TX and Claremont, CA. The pre-exponential and diffusion coefficients for the first term of the Gormley–Kennedy equation were estimated by regressing the log (nitrate mass deposited) against the axial distance from the entrance of the denuder. The field study average values of the two coefficients were compared by the two-tail *t*-test to the average values for the $HNO_3$–air system determined in the laboratory; the hypothesis that the means of the diffusion coefficients are equal may be rejected at the < 5% level of significance. The nitrate ion mass patterns in the denuder for the field cases do not adhere to the Gormley–Kennedy model applied to the simple $HNO_3$–air system. The source of excess nitrate deposited in the nylon tube could not be identified by this analysis. Candidate sources are deposition of gaseous N-compounds (analyzed as nitrate) other than nitric acid and release of nitric acid vapor from particles during transit in the denuder tube.

*Key word index*: Diffusion denuder, nitric acid, particulate nitrate, air pollution, sampling.

## 1. INTRODUCTION

Difference in diffusivity is an attractive approach to separate reactive gases and particles. Reactive gases may be separated from the particles by passing the aerosol through a conduit whose inner wall is a sink for the gas; the conduit is operated under conditions such that the trace reactive gas is collected with near 100% efficiency and the particles pass through the tube with near 100% efficiency. The reactive gas deposited in the tube may be recovered and the particles may be collected in an air stream free of that gas. A model of mass concentration depletion by diffusion through air for "perfect sink" tubes has been presented by Gormley and Kennedy (1949). Their series solution may be approximated for $C(x)/C(0) < 0.819$:

$$C(x)/C(0) = \alpha \exp(-11.49\, xD/Q) \qquad (1)$$

$$\alpha = 0.819$$

where $C(x)$ is the average concentration passing the axial distance x, $C(0)$ is concentration entering the tube, $D$ is the diffusion coefficient in air and $Q$ is the volumetric flow rate. Others have presented similar results for independent derivations (see review in Fuchs, 1964). Judeikis *et al.* (1978) have described the "imperfect sink" depletion tube, which may be operated to obtain gas–solid reaction rates. Previous applications of penetration analysis techniques have been: (a) to size condensation nuclei (see review in Fuchs, 1974; Marlow and Tanner, 1976); (b) to measure gaseous diffusion coefficients ($SO_3$, $NH_3$: Thomas, 1955; $I_2$: Browning and Ackley, 1962; $SO_2$: Fish and Durham, 1971; $HNO_3$: Durham and Stockburger, 1986); and (c) to examine gas-particle adsorption/desorption phenomena ($I_2/Al_2O_3$: Browning and Ackley, 1962; $SO_2$/Pt, $Fe_3O_4$, $Al_2O_3$: Smith *et al.*, 1969). Durham *et al.* (1984) in a unique application identified through penetration analysis the presence and concentration of sulfate-compound gases in the atmosphere.

The deposition patterns of trace reactive gases in aerosols being sampled in diffusion denuder tubes have been observed in some cases not to correspond to the Gormley–Kennedy equation (Smith *et al.*, 1969; Browning and Ackley, 1962). That behavior was likely due to gas-particle adsorption/desorption occurring in the denuder tube, which violates the Gormley–Kennedy assumption that the reactive gas must not be generated in the tube and that it be depleted only at the wall. In light of these examples of deviation, diffusion denuders used for atmospheric sampling should be subjected to an analysis of the deposition pattern of denuded gas to verify the adherence of the system to the Gormley–Kennedy model.

Reactive gas denuders have been developed for industrial hygiene surveys ($I_2$: Bennett and Adams, 1968), laboratory chemical measurements ($SO_2/SO_4^{2-}$: Durham *et al.*, 1978), and atmospheric monitoring ($NH_3$: Stevens *et al.*, 1978; Ferm, 1979). Recently, diffusion denuders have been configured for sampling atmospheric $HNO_3$ and nitrate-containing particles (for examples, see descriptions by: Appel *et al.*, 1981; Braman *et al.*, 1982; Eatough *et al.*, 1985; Forrest *et al.*, 1982; Possanzini *et al.*, 1983; Shaw *et al.*, 1982; Slanina *et al.*, 1982). Generally, researchers designing diffusion denuders have demonstrated in the laboratory the sampler's performance for $HNO_3$–air

systems. The type of evaluations were "exit function" analyses; the concentration of the stream entering and exiting the tube was measured for efficiencies > 95%. Larson and Taylor (1983) have performed an exit function analysis for 0.4-$\mu$m diameter $NH_4NO_3$ particles passed through a diffusion denuder. They did not observe changes in particle size distribution and mass concentration with an estimated error range of 0.01–6%, which is evidence that particulate nitrate evaporation did not occur. Forrest *et al.* (1982) performed similar exit function studies and also concluded that particulate nitrate evaporation does not occur in their diffusion denuder. Therefore, deviations from the Gormley–Kennedy equation are expected to be smaller than exit function analysis can detect.

We report our analysis of $HNO_3$ deposition patterns for a nylon-lined diffusion denuder operated in Riverside, CA in 1980, Houston, TX in 1980, and Claremont, CA in 1985. To interpret the patterns of atmospheric samples, it was necessary to demonstrate the adherence of the $HNO_3$ deposition patterns to the Gormley–Kennedy model as a function of relative humidity for particle-free air. Durham and Stockburger (1986) have shown that the deposition pattern of $HNO_3$ for 5–95% relative humidity is constant and in excellent agreement with the Gormley–Kennedy equation and semi-empirical diffusion theory. We have shown that the presence of $O_3$ does not alter the measured $HNO_3$ deposition patterns (Durham and Spiller, 1982). Joseph and Spicer (1978) reported that nylon does not react with NO, $NO_2$, PAN and organic nitrates. Sanhueza *et al.* (1984) reported that it does react with $HNO_2$, but did not establish whether an aqueous extraction produced nitrate ion. Thus, the extent of the contribution of $HNO_2$ to the nitrate deposition pattern on nylon is not known. Diffusive deposition of atmospheric particles does not make an important contribution to the deposition patterns of our denuder. Their diffusion coefficients are too small. Also, we find no evidence of the nylon liner electrically precipitating charged particles. Sulfate ion deposition patterns are frequently observed; they adhere to the Gormley–Kennedy equation with air diffusion coefficients (0.05–0.08 $cm^2\ s^{-1}$) corresponding to sulfate-compound gases (Durham *et al.*, 1984) and not particles.

## 2. THEORY

The governing assumptions of the truncated Gormley–Kennedy equation are: (1) the diffusion denuder is operated in well-developed laminar flow, (2) the reactive trace gas ($HNO_3$) is not generated in the tube or depleted except by diffusing and attaching to the wall, (3) $C(x)/C(0) < 0.819$, since the series solution has been truncated to one term. The differential form (Durham and Stockburger, 1986) of Equation (1) for the mass $M_j$ of the reactive trace gas deposited on the $j$th section is:

$$\ln M_j = \ln K - 11.49\,Dx/Q \tag{2}$$

where
$$K = \alpha M_T[-1 + \exp(11.49\,D\Delta x/Q)] \tag{3}$$

$\Delta x$ = the uniform section length, cm
$M_T$ = mass of reactive gas entering the denuder, $\mu$g.

In the regression analysis, the values of $\ln M_j$ in Equation (2) must be weighted to remove the improper influence of the more imprecise measurements (Bevington, 1969). The weighting factor is:

$$W_j = (M_j/s_j)^2 \tag{4}$$

where $s_j$ is the standard deviation of $M_j$.

The variation of temperature and pressure among experiments slightly influences the value of the $HNO_3$–air diffusion coefficient, which in turn influences the $HNO_3$ deposition pattern. That influence on the deposition pattern is eliminated by expressing the diffusion coefficient as a function of reference and experimental conditions (Durham and Stockburger, 1986), which is:

$$\gamma = 11.49\,(1/Q)(T/298)^{1.5}(1/P)x. \tag{5}$$

Thus, Equation (2) may be expressed as

$$\ln M_j = \ln K - D_0\gamma \tag{6}$$

where $K$ is unchanged, and $D_0$ is the diffusion coefficient at 298 K and 1 atm.

Through Equation (6) various experiments under different conditions of flow rate, temperature and pressure may be regressed to estimate the values of $\alpha$ and $D_0$ and compared directly.

## 3. EXPERIMENTAL

### *Analytical*

The complete sampler is shown in Fig. 1, but the focus of this paper is only on the performance of the nylon denuder section. A detailed schematic of the denuder is shown in Fig. 2. Nylon diffusion denuder tubes were made by lining the inner surface of a Teflon tube (inner diameter = 0.93 cm) with strips of nylon-fiber mats (M-8PL00201, Ghia Corporation, Pleasanton, CA) of thickness 0.15 mm. The Teflon tube was kept straight by inserting it into a close-fitting rigid steel tube. Since parabolic flow is a condition for Equations (1), (2) and (6) for diffusional collection, a 25-cm section of inert Teflon surface was left bare upstream of the reactive nylon liner collecting surface. The parabolic profile is fully established 21 cm from the entrance of the Teflon tube for a flow rate of 25 $cm^3\ s^{-1}$, which corresponds to a Reynolds number of 235 for this denuder. Thus, the Gormley–Kennedy flow conditions are fully satisfied for this and smaller flow rates. The diffusion denuder was operated into a vertical position to eliminate biases from particle settling. A cyclone with collection efficiency of 50% for 2.1 $\mu$m diameter particles at a flow rate of 28 $\ell\ min^{-1}$ eliminated coarse particles from the sample stream for the denuder. The cyclone was tapped at the bottom, and the particles captured were delivered to a filter maintained at a flow rate of 0.5 $\ell\ min^{-1}$. This design prevented a positive bias for $HNO_3$ due to evaporation of the large particles collected by the cyclone. The sampling system

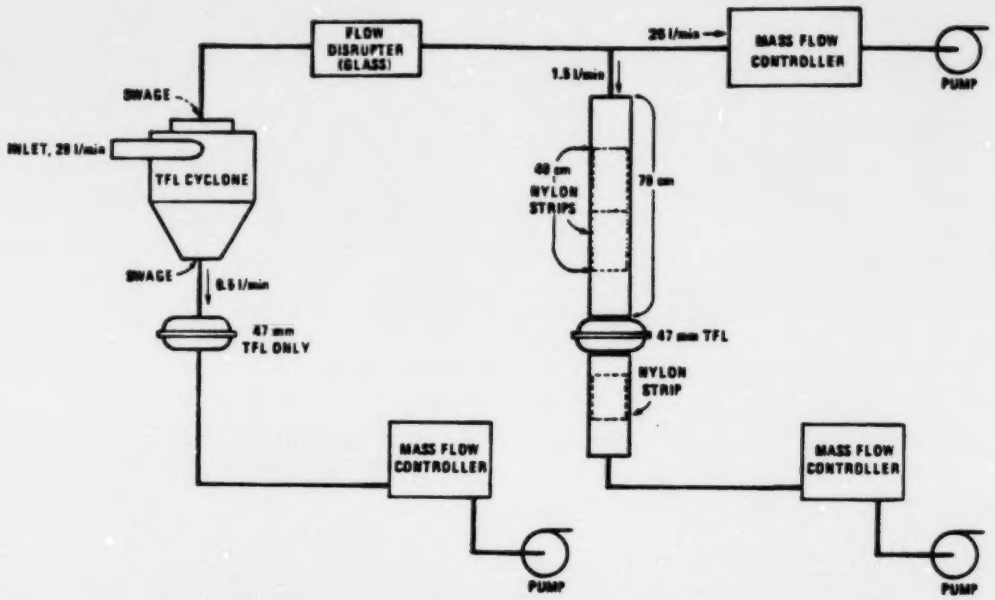


Fig. 1. Nitric acid diffusion-denuder sampling system. The ambient aerosol is pumped at 28 $l\,min^{-1}$ through the Teflon (TFL) cyclone. Particles greater than about 2.5 $\mu m$ exit through the bottom of the cyclone and are collected with a constant flowrate of 0.5 $l\,min^{-1}$. The smaller particles exit through the top of the cyclone and pass through a flow disrupter to remove swirl. After the flow disrupter, a sample is pulled at 1.5 $l\,min^{-1}$ through the diffusion denuder, which is a Teflon pipe with a nylon film liner (see Fig. 2).

was operated in a standard Hi-Vol shelter to shield against direct sunlight and precipitation.

After sample collection, the nylon liners were removed and cut into eight sections of $5.00 \pm 0.05$ cm each. Each section was extracted in 10 $cm^3$ of an aqueous solution of 0.003 M $NaHCO_3$ and 0.0024 M $Na_2CO_3$, which was the eluent solution for the ion chromatograph. The extraction was expedited by vortex agitation. The nitrate and sulfate concentrations of the extracts were determined by injecting aliquots into a Dionex Ion Chromatograph Model 14. The ion peaks were integrated and concentrations calculated based on 0.5 $\mu g\,cm^{-3}$ calibration standards. The standard deviation for replicates over the observed concentration range of 0.01–3 $\mu g\,cm^{-3}$ was the greater of $\pm 0.03\ \mu g\,cm^{-3}$ or $\pm 3\%$. The variance of the deposition pattern is dominated by the analytical variance. The variances of flow rate and sectioning the nylon liner were conservatively accounted for by setting the overall standard deviation of $M_j$ to be twice the chemical analysis standard deviation. That is, the system standard deviation is the greater of $\pm 0.6\ \mu g$ section$^{-1}$ or $\pm 6\%$.

The nitrate blank values for the nylon were typically $0.03 \pm 0.01\ \mu g\,cm^{-3}$ for the 10 $cm^3$ extract. Precision of the nitrate determination was maintained at $\pm 0.03\ \mu g\,cm^{-3}$ or 3% by re-analyzing the standard after every fourth sample.

*Field sites*

Riverside, California: the State Wide Air Pollution Research Center, Fawcett Laboratory.

Claremont, California: a vacant parking lot on the campus of Pomona College.

Houston, Texas: the Houston Air Pollution Monitoring Site located at the intersection of Crawford and Polk Streets.

## 4. RESULTS

The nitrate patterns for denuder samples collected in Riverside, CA in 1980 for 12 days are shown in Table 1. The experimental measurements are compared to those expected for the gaseous $HNO_3$ depletion. To calculate the gaseous $HNO_3$ profile from Equations (3) and (6), the value of $M_T$ must be estimated. We assumed that particulate $NO_3^-$ is fully conserved for the first section of the denuder, and that the only species deposited is $HNO_3$. Thus, $M_T$ for gaseous $HNO_3$ entering the denuder is:

$$M_T = M_1/(\text{fractional deposition to } M_1) \quad (7)$$
$$= M_1/[1 - 0.819 \exp(D_0\gamma(1))]$$

where $\gamma(1)$ is the value of $\gamma$ for the first section ($x = 5$ cm) with collected $NO_3^-$ mass $M_1$. Durham and Stockburger (1986) demonstrated experimentally that Equation (7) is valid for the gaseous $HNO_3$–air ($5 < RH < 95\%$) system. In accordance with that assumption, "excess" deposited nitrate is shown in Table 1 as zero for section 1 in all cases. For sections 2–8, the "excess" is the difference between the measured mass and that calculated for the $HNO_3$–air system. The excess nitrate mass is positive for every section, except No. 3 for 9/25/80, which is inconsistent with the progression of $M_j$ and appears to be due to experimental error. The range of total excess nitrate was $16 \pm 4\%$

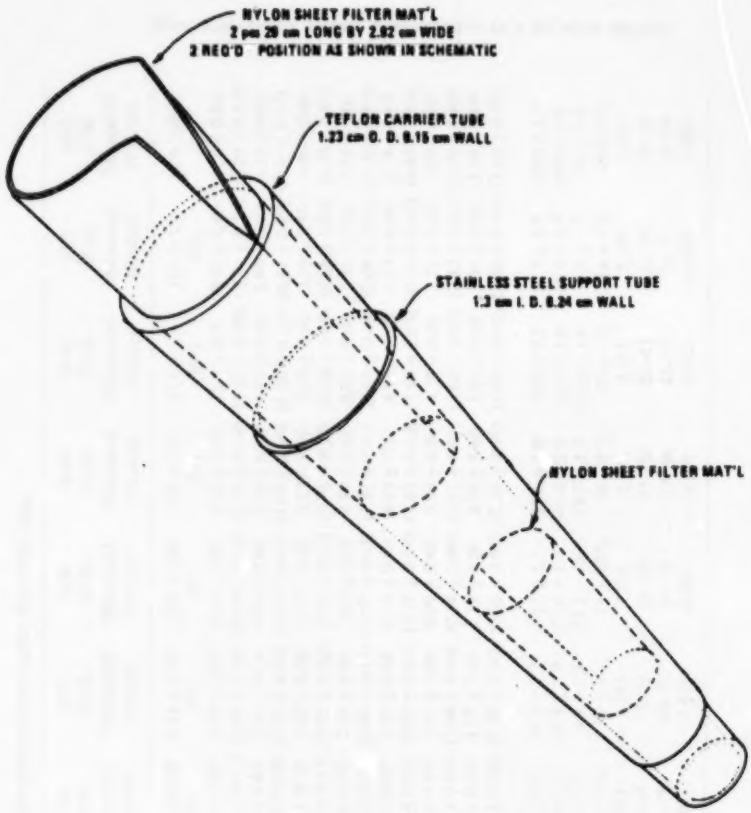
NYLON SHEET FILTER MAT'L
2 pcs 29 cm LONG BY 2.82 cm WIDE
2 REQ'D POSITION AS SHOWN IN SCHEMATIC
TEFLON CARRIER TUBE
1.23 cm O. D. 0.15 cm WALL
STAINLESS STEEL SUPPORT TUBE
1.3 cm I. D. 0.24 cm WALL
NYLON SHEET FILTER MAT'L

Fig. 2. Nitric acid denuder tube.

to 95 ± 22% of the theoretical estimated value of $M_T$ for the $HNO_3$–air system. There are insufficient cases to reveal dependences of the excess mass on relative humidity and temperature.

The detailed nitrate deposition data for the Houston 1980, Claremont 1985 and Riverside 1980 have experimental and excess mass patterns that are similar to those shown in Table 1. The nitrate deposition patterns have been regressed against Equation (6), with the data weighted as shown in Equation (4), to obtain estimates of $K$ and $D_0$. $K$ is a function of $\alpha$ and $M_T$; to estimate $\alpha$, the value of $M_T$ must be known. Since we had no direct measurement of the free $HNO_3$ vapor concentration, it was necessary to estimate $M_T$ from the denuder tube. For the $HNO_3$–air system, we can estimate $M_T$ from the $NO_3^-$ mass on one [e.g. Equation (7)] or more sections. Our tube is operated to collect about 90% of $M_T$ for the $HNO_3$–air system. Thus, if it is performing in accordance with the Gormley–Kennedy assumptions,

$$M_T' = (M_1 + \ldots + M_8)/0.90. \quad (8)$$

The estimates of $M_T$ through Equation (8) result in the estimates of $\alpha$ (given in Table 2) that are the nearest to the theoretical value of 0.819. The estimate of $D_0$ does not depend on the mass of gaseous $HNO_3$ entering the denuder, and the values of $D_0$ in Table 2 are valid estimates.

The laboratory $HNO_3$–air system's variance-weighted averages of $\alpha$ and $D_0$ are shown in Table 2 for comparison with each of their field cases and the averages.

For all of the field cases, the experimentally determined values of $M_j$ ($j$ = 2–8) exceeded those predicted for the $HNO_3$–air system where the gaseous $HNO_3$ mass ($M_T$) entering the denuder was estimated from $M_1$ through Equation (7). Also, the mass ($M_T'$) entering may be estimated through Equation (8). The estimates of $M_T$ and $M_T'$ are given in Table 2. From the values of $[(M_T' - M_T)/M_T](100)$, it is seen that $M_T'$ (derived from the total mass deposited in the denuder) generally exceeds $M_T$. For the two cases in which that is not so, the estimated error is greater than the mean.

## 5. DISCUSSION

The field results for Riverside 1980, Houston 1980 and Claremont 1985 have been combined to produce variance- and mass-weighted estimates of $\alpha$ and $D_0$, which are given in Table 2. Variance weighting gives more importance in estimating the regression coef-

Table 1. Riverside, CA $HNO_3$ denuder deposition patterns and excess deposited mass

| Date, 1980: | 9/15 | 9/17 | 9/22 | 9/24 | 9/25 | 9/26 | 9/27 | 9/28 | 9/29 | 9/30 | 10/1 | 10/2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start time, PST: | 1200 | 0000 | 0730 | 0730 | 0730 | 0730 | 0730 | 0730 | 0730 | 0730 | 0730 | 0730 |
| Mass deposited (μg): | Measured | Measured | Measured | Measured | Measured | Measured | Measured | Measured | Measured | Measured | Measured | Measured |
| Section | (Excess) | (Excess) | (Excess) | (Excess) | (Excess) | (Excess) | (Excess) | (Excess) | (Excess) | (Excess) | (Excess) | (Excess) |
| 1 | 5.08 ± 0.60 | 12.8 ± 0.8 | 3.11 ± 0.60 | 12.2 ± 0.7 | 11.5 ± 0.7 | 8.67 ± 0.60 | 8.21 ± 0.60 | 6.89 ± 0.60 | 17.0 ± 1.0 | 23.8 ± 1.4 | 18.2 ± 1.1 | 12.0 ± 0.7 |
| | (0*) | (0*) | (0*) | (0*) | (0*) | (0*) | (0*) | (0*) | (0*) | (0*) | (0*) | (0*) |
| 2 | 3.60 ± 0.60 | 6.23 ± 0.60 | 2.17 ± 0.60 | 6.43 ± 0.60 | 5.16 ± 0.60 | 5.30 ± 0.60 | 4.50 ± 0.60 | 3.43 ± 0.60 | 9.24 ± 0.60 | 12.3 ± 0.7 | 8.90 ± 0.60 | 5.78 ± 0.60 |
| | (1.49 ± 0.65) | (0.90 ± 0.68) | (0.88 ± 0.65) | (1.35 ± 0.67) | (0.36 ± 0.67) | (1.69 ± 0.65) | (1.08 ± 0.68) | (0.56 ± 0.65) | (2.15 ± 0.74) | (2.35 ± 0.74) | (1.31 ± 0.75) | (0.80 ± 0.67) |
| 3 | 3.28 ± 0.60 | 4.85 ± 0.60 | 1.85 ± 0.60 | 5.31 ± 0.60 | 2.72 ± 0.60 | 3.53 ± 0.60 | 3.12 ± 0.60 | 5.00 ± 0.60 | 7.00 ± 0.60 | 8.75 ± 0.60 | 5.94 ± 0.60 | 5.25 ± 0.60 |
| | (1.67 ± 0.63) | (0.79 ± 0.67) | (0.86 ± 0.63) | (1.43 ± 0.64) | (−0.94 ± 0.64) | (0.78 ± 0.63) | (0.51 ± 0.63) | (2.81 ± 0.63) | (1.60 ± 0.68) | (1.18 ± 0.75) | (0.14 ± 0.69) | (1.45 ± 0.64) |
| 4 | 2.68 ± 0.60 | 4.08 ± 0.60 | 1.78 ± 0.60 | 4.29 ± 0.60 | 7.24 ± 0.60 | 5.72 ± 0.60 | 2.64 ± 0.60 | 4.37 ± 0.60 | 5.83 ± 0.60 | 7.05 ± 0.60 | 5.29 ± 0.60 | 4.10 ± 0.60 |
| | (1.45 ± 0.62) | (0.99 ± 0.63) | (1.02 ± 0.62) | (1.33 ± 0.63) | (4.44 ± 0.62) | (3.62 ± 0.62) | (0.65 ± 0.62) | (2.69 ± 0.62) | (1.71 ± 0.65) | (1.28 ± 0.69) | (0.86 ± 0.66) | (1.20 ± 0.62) |
| 5 | 2.21 ± 0.60 | 3.27 ± 0.60 | 1.78 ± 0.60 | 3.46 ± 0.60 | 4.40 ± 0.60 | 2.30 ± 0.60 | 2.41 ± 0.60 | 3.87 ± 0.60 | 4.96 ± 0.60 | 6.47 ± 0.60 | 5.46 ± 0.60 | 3.53 ± 0.60 |
| | (1.27 ± 0.61) | (0.92 ± 0.62) | (1.20 ± 0.61) | (1.20 ± 0.62) | (2.26 ± 0.61) | (0.70 ± 0.61) | (0.89 ± 0.61) | (2.59 ± 0.61) | (1.82 ± 0.63) | (2.07 ± 0.66) | (2.08 ± 0.63) | (1.32 ± 0.61) |
| 6 | 3.02 ± 0.60 | 2.59 ± 0.60 | 1.55 ± 0.60 | 3.43 ± 0.60 | 3.60 ± 0.60 | 1.96 ± 0.60 | 2.10 ± 0.60 | 4.74 ± 0.60 | 4.05 ± 0.62 | 4.81 ± 0.60 | 3.13 ± 0.60 | 2.74 ± 0.60 |
| | (2.30 ± 0.61) | (0.80 ± 0.61) | (1.11 ± 0.61) | (1.70 ± 0.61) | (1.97 ± 0.61) | (0.73 ± 0.61) | (0.94 ± 0.61) | (3.76 ± 0.61) | (1.65 ± 0.62) | (1.45 ± 0.63) | (0.55 ± 0.62) | (1.05 ± 0.61) |
| 7 | 2.11 ± 0.60 | 2.29 ± 0.60 | 1.09 ± 0.60 | 2.76 ± 0.60 | 2.93 ± 0.60 | 1.93 ± 0.60 | 1.95 ± 0.60 | 0.99 ± 0.60 | 3.94 ± 0.60 | 4.24 ± 0.60 | 2.79 ± 0.60 | 3.04 ± 0.60 |
| | (1.56 ± 0.60) | (0.92 ± 0.61) | (0.75 ± 0.60) | (1.44 ± 0.61) | (1.68 ± 0.60) | (0.99 ± 0.60) | (1.06 ± 0.60) | (0.24 ± 0.60) | (2.11 ± 0.61) | (1.68 ± 0.62) | (0.82 ± 0.61) | (1.75 ± 0.60) |
| 8 | 2.29 ± 0.60 | 2.14 ± 0.60 | 1.97 ± 0.60 | 2.06 ± 0.60 | 2.36 ± 0.60 | 1.67 ± 0.60 | 1.97 ± 0.60 | 1.13 ± 0.60 | 3.56 ± 0.60 | 3.41 ± 0.60 | 3.01 ± 0.60 | 2.59 ± 0.60 |
| | (1.87 ± 0.60) | (1.10 ± 0.60) | (1.71 ± 0.60) | (1.05 ± 0.60) | (1.41 ± 0.60) | (0.96 ± 0.60) | (1.29 ± 0.60) | (0.56 ± 0.60) | (2.16 ± 0.61) | (1.46 ± 0.61) | (1.50 ± 0.61) | (1.60 ± 0.60) |
| **Total mass (μg)** | | | | | | | | | | | | |
| Measured: | 24.3 ± 1.7 | 38.2 ± 1.8 | 15.3 ± 1.7 | 39.7 ± 1.7 | 39.9 ± 1.7 | 31.0 ± 1.7 | 26.9 ± 1.7 | 30.3 ± 1.7 | 55.6 ± 1.9 | 70.8 ± 2.2 | 52.7 ± 1.9 | 39.0 ± 1.7 |
| Theory:† | 12.9 ± 0.9 | 32.5 ± 1.5 | 7.9 ± 0.9 | 31.1 ± 1.4 | 29.4 ± 1.3 | 22.4 ± 1.2 | 20.9 ± 1.3 | 17.6 ± 1.0 | 43.3 ± 1.5 | 60.7 ± 1.9 | 46.5 ± 1.7 | 30.6 ± 1.4 |
| Excess (μg)‡ | 11.6 ± 1.5 | 6.4 ± 1.6 | 7.5 ± 1.5 | 9.5 ± 1.7 | 11.2 ± 1.8 | 9.5 ± 1.6 | 6.4 ± 1.6 | 13.2 ± 1.6 | 13.2 ± 1.7 | 11.5 ± 1.8 | 7.3 ± 1.7 | 9.2 ± 1.6 |
| % | 90 ± 13% | 20 ± 5% | 95 ± 22% | 31 ± 6% | 38 ± 6% | 42 ± 7% | 31 ± 8% | 75 ± 10% | 30 ± 4% | 19 ± 3% | 16 ± 4% | 30 ± 5% |
| $\gamma(1)$ (cm$^{-2}$ s): | 2.283 | 2.306 | 2.283 | 2.285 | 2.283 | 2.287 | 2.283 | 2.276 | 2.295 | 2.295 | 2.285 | 2.287 |
| Temperature (°C): | 17–24 | 16–24 | 16–27 | 18–36 | 18–35 | 19–34 | 18–33 | 18–34 | 21–40 | 22–43 | 20–44 | 20–39 |
| Relative humidity (%): | 38–90 | 62–86 | 55–92 | 25–75 | 25–80 | 40–78 | 40–79 | 27–75 | 27–56 | 43–53 | 26–73 | 12–84 |
| Pressure (atm.): | 1.000 | 1.000 | 0.997 | 0.997 | 0.997 | 0.997 | 0.997 | 0.997 | 0.997 | 0.997 | 0.997 | 1.000 |

*Assumption = there is no excess mass on the first section.
† Sum of theoretical estimate for $HNO_3$–air system.
‡ (Measured mass) – (theoretical estimate) for the denuder.

Table 2. Estimation of $\alpha$ and $D_0$ from regression of Equation (6) for the $HNO_3$ denuder tube

| Experiment | $\alpha$ | $D_0$ ($cm^2\ s^{-1}$) | $M_1$ ($\mu g$) | $M'_T$ ($\mu g$) [eqn (8)] | $M_T$ ($\mu g$) [eqn (7)] | $(M'_T - M_T)/M_T \times 100$ | Sample volume ($m^3$) |
|---|---|---|---|---|---|---|---|
| Laboratory | | | | | | | |
| $HNO_3$–air, 5 < RH < 95%* ($n = 7$) | $0.829 \pm 0.012$ | $0.118 \pm 0.003$ | | | | | |
| Field: Riverside, CA, 1980 | | | | | | | |
| (start date and time; duration) | † | | | | | | |
| 9/15 1200 PST; 24 h | $1.9 \pm 1.0$ | $0.032 \pm 0.018$ | $5.08 \pm 0.60$ | $27.0 \pm 1.9$ | $14.3 \pm 1.7$ | $89 \pm 18$ | 2.12 |
| 9/17 0000 PST; 24 h | $0.98 \pm 0.30$ | $0.086 \pm 0.015$ | $12.8 \pm 0.8$ | $42.4 \pm 1.9$ | $35.8 \pm 2.1$ | $18 \pm 8$ | 2.10 |
| 9/22 0730 PST; 24 h | $3.8 \pm 3.7$ | $0.014 \pm 0.026$ | $3.11 \pm 0.60$ | $17.0 \pm 1.9$ | $8.7 \pm 1.7$ | $95 \pm 29$ | 2.13 |
| 9/24 0730 PST; 24 h | $1.06 \pm 0.32$ | $0.075 \pm 0.013$ | $12.2 \pm 0.7$ | $44.3 \pm 1.9$ | $34.3 \pm 2.1$ | $29 \pm 8$ | 2.20 |
| 9/25 0730 PST; 24 h | $1.53 \pm 0.57$ | $0.048 \pm 0.014$ | $11.5 \pm 0.7$ | $44.3 \pm 1.9$ | $32.5 \pm 2.0$ | $36 \pm 8$ | 2.19 |
| 9/26 0730 PST; 24 h | $1.22 \pm 0.43$ | $0.077 \pm 0.018$ | $8.67 \pm 0.60$ | $34.6 \pm 1.9$ | $24.4 \pm 1.7$ | $42 \pm 10$ | 2.19 |
| 9/27 0730 PST; 24 h | $1.12 \pm 0.50$ | $0.066 \pm 0.018$ | $8.21 \pm 0.60$ | $29.9 \pm 1.9$ | $23.1 \pm 1.7$ | $29 \pm 11$ | 2.18 |
| 9/28 0730 PST; 24 h | $4.4 \pm 2.4$ | $0.014 \pm 0.018$ | $6.89 \pm 0.60$ | $33.8 \pm 1.9$ | $19.4 \pm 1.7$ | $74 \pm 13$ | 2.20 |
| 9/29 0730 PST; 24 h | $1.06 \pm 0.22$ | $0.075 \pm 0.009$ | $17.0 \pm 1.0$ | $61.8 \pm 2.1$ | $47.8 \pm 2.9$ | $29 \pm 7$ | 2.22 |
| 9/30 0730 PST; 24 h | $0.95 \pm 0.17$ | $0.092 \pm 0.008$ | $23.8 \pm 1.4$ | $78.7 \pm 2.4$ | $66.9 \pm 4.0$ | $17 \pm 7$ | 2.24 |
| 10/1 0730 PST; 24 h | $0.98 \pm 0.22$ | $0.084 \pm 0.011$ | $12.7 \pm 0.7$ | $58.7 \pm 2.1$ | $51.3 \pm 3.1$ | $14 \pm 7$ | 2.26 |
| 10/2 0730 PST; 24 h | $1.13 \pm 0.38$ | $0.063 \pm 0.013$ | $18.2 \pm 1.1$ | $43.3 \pm 1.9$ | $33.6 \pm 2.0$ | $29 \pm 8$ | 2.22 |
| Variance-weighted average: | $1.05 \pm 0.09$ | $0.071 \pm 0.004$ | | | | | |
| Mass-weighted average: | $1.44 \pm 0.05$ | $0.069 \pm 0.006$ | | | | | |
| Field: Claremont, CA, 1985 | | | | | | | |
| (start date and time; duration) | † | | | | | | |
| 9/12 0830 PDT; 47.63 h‡ | $0.838 \pm 0.080$ | $0.156 \pm 0.010$ | $33.9 \pm 2.0$ | $105 \pm 3$ | $95.0 \pm 5.7$ | $11 \pm 7$ | 4.14 |
| 9/12 2101 PDT; 45.75 h§ | $0.88 \pm 0.30$ | $0.181 \pm 0.062$ | $5.30 \pm 0.60$ | $14.8 \pm 1.9$ | $14.9 \pm 1.7$ | $-1 \pm 17$ | 3.98 |
| 9/16 1122 PDT; 70.63 h | $1.03 \pm 0.33$ | $0.082 \pm 0.022$ | $8.11 \pm 0.60$ | $28.3 \pm 1.9$ | $22.7 \pm 1.7$ | $25 \pm 11$ | 5.79 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 10/2 0730 PST; 24 h | 1.13 ± 0.38 | 0.063 ± 0.013 | 18.2 ± 1.1 | 43.3 ± 1.9 | 33.0 ± 2.0 | 27 ± 8 | 2.22 |
| Variance-weighted average: | 1.05 ± 0.09 | 0.071 ± 0.004 | | | | | |
| Mass-weighted average: | 1.44 ± 0.05 | 0.069 ± 0.006 | | | | | |
| Field: Claremont, CA, 1985 | | | | | | | |
| (start date and time; duration) | | | | | | | |
| | † | | | | | | |
| 9/12 0830 PDT; 47.63 h‡ | 0.838 ± 0.080 | 0.156 ± 0.010 | 33.9 ± 2.0 | 105 ± 3 | 95.0 ± 5.7 | 11 ± 7 | 4.14 |
| 9/12 2101 PDT; 45.75 h§ | 0.88 ± 0.30 | 0.181 ± 0.062 | 5.30 ± 0.60 | 14.8 ± 1.9 | 14.9 ± 1.7 | −1 ± 17 | 3.98 |
| 9/16 1122 PDT; 70.63 h | 1.03 ± 0.3 | 0.082 ± 0.022 | 8.11 ± 0.60 | 28.3 ± 1.9 | 22.7 ± 1.7 | 25 ± 11 | 5.79 |
| Variance-weighted average: | 0.851 ± 0.0[illegible]5 | 0.144 ± 0.009 | | | | | |
| Mass-weighted average: | 0.88 ± 0.1[illegible] | 0.144 ± 0.017 | | | | | |
| Field: Houston, TX, 1980 | | | | | | | |
| (start date and time; duration) | | | | | | | |
| | † | | | | | | |
| 9/17 2300 CST; ? | 1.0 ± 12 | 0.078 ± 0.730 | 1.18 ± 0.60 | 2.0 ± 1.9 | 3.2 ± 1.7 | −37 ± 75 | ? |
| 9/18 2350 CST; 24 h | 4.65 ± 0.92 | 0.011 ± 0.005 | 14.0 ± 0.8 | 67.8 ± 1.7 | 39.3 ± 2.4 | 72 ± 7 | 2.16 |
| 9/19 2200 CST; ? | 6.6 ± 5.1 | 0.007 ± 0.020 | 3.20 ± 0.60 | 16.3 ± 1.9 | 8.93 ± 1.7 | 82 ± 28 | ? |
| 9/24 2005 CST; 24 h | 1.23 ± 0.51 | 0.069 ± 0.019 | 7.63 ± 0.60 | 23.8 ± 1.9 | 21.3 ± 1.7 | 12 ± 12 | 2.16 |
| 9/30 2145 CST; 24 h | 2.28 ± 0.90 | 0.023 ± 0.011 | 7.71 ± 0.60 | 32.4 ± 1.9 | 21.6 ± 1.7 | 50 ± 12 | 2.16 |
| 10/3 0830 CST; 24 h | 3.9 ± 2.8 | 0.013 ± 0.018 | 5.36 ± 0.60 | 19.9 ± 1.9 | 15.0 ± 1.7 | 33 ± 17 | 2.16 |
| 10/11 2125 CST; 24 h | 2.55 ± 0.81 | 0.024 ± 0.009 | 7.03 ± 0.60 | 36.4 ± 1.9 | 19.6 ± 1.7 | 86 ± 13 | 2.16 |
| 10/13 2015 CST; 24 h | −23 ± 10 | −0.002 ± 0.011 | 5.87 ± 0.60 | 31.7 ± 1.9 | 16.5 ± 1.7 | 92 ± 15 | 2.16 |
| 10/14 2140 CST; 24 h | −1.1 ± 1.7 | −0.032 ± 0.03 | 1.79 ± 0.60 | 10.7 ± 1.9 | 5.0 ± 1.7 | 114 ± 51 | 2.16 |
| 10/15 2205 CST; ? | −1.5 ± 4.2 | −0.024 ± 0.054 | 1.15 ± 0.60 | 6.1 ± 1.9 | 3.2 ± 1.7 | 91 ± 80 | ? |
| 10/21 2120 CST; 24 h | 1.51 ± 0.52 | 0.039 ± 0.011 | 8.17 ± 0.60 | 32.8 ± 1.9 | 23.0 ± 1.7 | 43 ± 11 | 2.16 |
| 10/22 2140 CST; 24 h | 1.74 ± 0.23 | 0.035 ± 0.004 | 20.5 ± 1.2 | 90.3 ± 5.4 | 57.3 ± 3.4 | 58 ± 11 | 2.16 |
| 10/23 2150 CST; 24 h | 7.1 ± 2.9 | 0.006 ± 0.010 | 6.50 ± 0.60 | 32.0 ± 1.9 | 18.3 ± 1.7 | 75 ± 14 | 2.16 |
| Variance-weighted average: | 1.70 ± 0.18 | 0.023 ± 0.002 | | | | | |
| Mass-weighted average: | 0.7 ± 1.9 | 0.021 ± 0.014 | | | | | |

*From Durham and Stockburger (1986).
†Estimated using Eqn (8); values estimated from Eqn (7) are larger.
‡Daylight hours only.
§Night hours only.

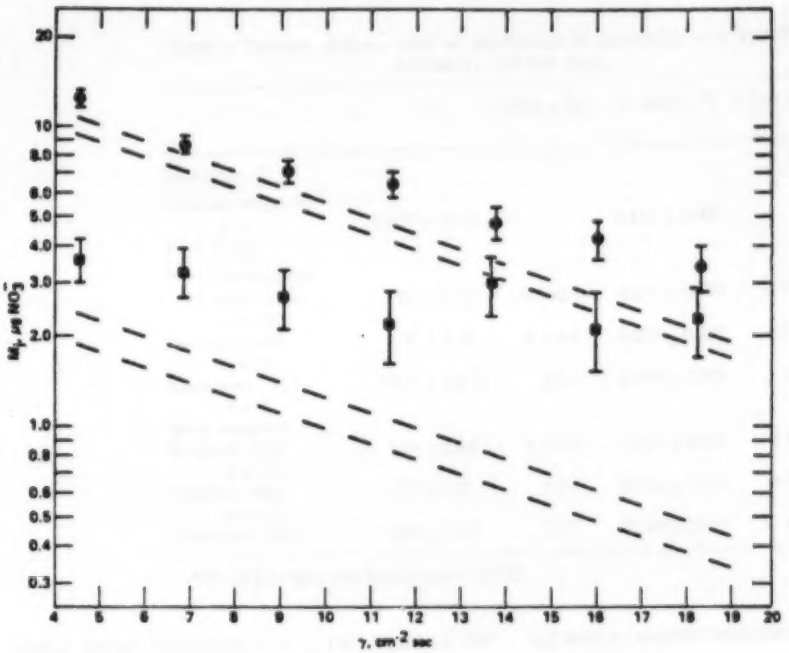


Fig. 3. Nitrate deposition patterns (Riverside) in the nylon denuder. The top profile is for the sample taken 30 September 1980, and the bottom profile for 15 September 1980. The points are the nitrate mass recovered from the section and plotted at its exit coordinate. The overall estimated system standard deviations are indicated. The profiles begin with section 2 ($\gamma = 4.5\ cm^{-2}$ s, which is $x = 10$ cm) since Equation (6) excludes the first section. The dashed lines correspond to the nitrate deposition pattern ($\pm 1\sigma$) of the $HNO_3$–air system, as predicted from the measured $M_1$. In $\gamma$-coordinates, the dashed lines have slopes of $-D_0$ and the intercept on the $M_1$-axis is ln $K$. The regression lines for the two atmospheric samples are not plotted, but the estimates of $\alpha$ and $D_0$ are presented in Table 2.

ficients to the cases with greater precision. For documenting $HNO_3$ concentration trends, however, sampler performance at the higher pollutant concentrations may be more important; mass-weighting emphasizes those cases in forming the averages. The significance of the differences of $\alpha$ and $D_0$ for the laboratory and field cases has been examined by the two-tail Student $t$-test, and the results are presented in Table 3. For all field cases, the hypothesis that the means of $D_0$ are equal to the laboratory derived mean value may be rejected at the $< 5\%$ level of significance. Although the means of $\alpha$ for the other cases cannot be rejected at the 5% level of significance, their corresponding means of $D_0$ may be rejected. Thus, for the field cases, the nylon denuder does not adhere to the Gormley–Kennedy model of the simple $HNO_3$–air system characterized in the laboratory. Mulawa and Cadle (1985) investigated the atmospheric $HNO_3^-$ particulate $NO_3^-$ system in Warren, Michigan with a sampler similar to ours. Their penetration analysis indicates that the atmospheric system does not adhere to the Gormley–Kennedy model.

Our analysis cannot identify the sources of nitrate that produce the excess deposited nitrate mass patterns. A notable feature of the excess deposition profiles is that they do not exhibit definitive exponential decay. Two likely source candidates are (a) contributions from other N-compounds such as $HNO_2$ and organic nitrates for which nylon is not a "perfect sink", and (b) evaporation of $HNO_3$ from the particles during transit in the denuder. $HNO_2$ may be taken up by the nylon and may produce (or substantially contribute to) the excess deposited nitrate. It is not known if nylon is a "perfect sink" for $HNO_2$. Assuming it is, and that the $HNO_2$–air diffusion coefficient calculated from semi-empirical theory (Gilliland, 1934) is 0.128 $cm^2\ s^{-1}$, the divergence of the $HNO_3$ and $HNO_2$ patterns grows as distance down the denuder increases and is the greatest at the eighth section. If the gases are perfectly adsorbed, the fractional deposition to the eighth section for $HNO_3$ is 0.0291 and for $HNO_2$ is 0.0266; that corresponds to a 0.25% divergence in deposition function; our denuder cannot resolve the deposition patterns for $HNO_3$ and $HNO_2$ if gaseous $HNO_2$ is perfectly adsorbed. Thus, $HNO_2$, if perfectly adsorbed, cannot be the source of the excess nitrate deposition in our denuder. $HNO_2$ would only be a candidate for the general cause of the

Table 3. Two-tail Student *t*-test of significance of differences of $\alpha$ and $D_0$ for laboratory and field cases

| | $\alpha$ | $2\,Pr(t > \Delta\alpha)$ | $D_0$ (cm$^2$ s$^{-1}$) | $2\,Pr(t > \Delta D_0)$ |
|---|---|---|---|---|
| Laboratory* | | | | |
| Variance-weighted $n = 7$ | $0.829 \pm 0.012$ | | $0.118 \pm 0.003$ | |
| Field study | | | | |
| Variance-weighted | | | | |
| Riverside 1980 $n = 12$ | $1.05 \pm 0.09$ | $< 0.001$ | $0.071 \pm 0.004$ | $< 0.001$ |
| Houston 1980 $n = 13$ | $1.70 \pm 0.18$ | $< 0.001$ | $0.023 \pm 0.002$ | $< 0.001$ |
| Claremont 1985 $n = 3$ | $0.851 \pm 0.075$ | 0.63 | $0.144 \pm 0.009$ | 0.001 |
| Mass-weighted | | | | |
| Riverside 1980 $n = 12$ | $1.44 \pm 0.05$ | $< 0.001$ | $0.069 \pm 0.006$ | $< 0.001$ |
| Houston 1980 $n = 13$ | $0.7 \pm 1.9$ | 0.81 | $0.021 \pm 0.014$ | $< 0.001$ |
| Claremont 1985 | $0.88 \pm 0.15$ | 0.57 | $0.144 \pm 0.017$ | 0.03 |

* From Durham and Stockburger (1986).

excess nitrate deposition if it is demonstrated that nylon is not a perfect sink for $HNO_2$.

## 6. SUMMARY AND CONCLUSIONS

The technique of penetration analysis for ambient samples has been applied to an $HNO_3$–air diffusion denuder previously shown to adhere to the Gormley–Kennedy model equation; suspected sources of bias (relative humidity, $O_3$) were demonstrated not to be important. However, the ambient samples collected with the diffusion denuder in Riverside, California, Houston, Texas and Claremont, California exhibited $NO_3^-$ mass profiles that do not adhere to the model equation. These results are suggested to be due to (a) the release of $HNO_3$ vapor from particles during transit in the denuder, or (b) the deposition of another N-compound that is extracted and analyzed as $NO_3^-$.

Our results do not establish the source of non-ideal behavior for nylon denuders. If the source is $HNO_3$ release from particulate $NO_3^-$, $HNO_3$ diffusion denuder samplers may exhibit a substantial bias. Instead, if the source of non-ideal behavior is another N-compound (e.g. $HNO_2$), it indicates a general problem with all systems that sample $HNO_3$ and particulate $NO_3^-$ with nylon.

We recommend that investigators sampling reactive aerosols with a diffusion denuder analyze the sampler's deposition profiles for the relevant species to determine if their sampler performs according to its theoretical model equation. Such critical analysis of deposition profiles seems to be capable of detecting unexpected performance factors.

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